Fabrication of Interdigitated Carbon Structures by Laser Pyrolysis of Photoresist

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A technique to produce carbon by pyrolysis of a positive photoresist on a silicon substrate using a laser beam (laser pyrolysis) is described. The characteristics of the two-dimensional carbon microstructures produced are determined by the motion and power of the laser beam as it traverses the surface of the photoresist. This approach has advantages over conventional photolithography, which was used to pattern photoresists that were then converted to carbon by thermal pyrolysis. Examples of Raman spectra and carbon structures obtained by laser pyrolysis are presented.
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Carbonaceous materials are widely used in electrochemical systems such as batteries and fuel cells. The precursors for carbon are as varied as the types of carbons that are available. For example, precursors include petroleum, natural products, hydrocarbon gases, and biomass. Carbons are generally produced from these materials by thermal treatment. In many cases, the properties of the final product are not easily controlled, with variations in particle size, surface area, and particle morphology present. Over the past several years,[1-3] we have been investigating the preparation of well-defined carbon structures obtained by heating photoresists that are commonly used in the semiconductor industry. In one phase of this effort,[4-8] the photoresist was spin coated on silicon wafers, and then heated in an inert environment in temperatures ranging from 600 to 1100°C to form thin carbon films (less than 10 μm thick). The properties of the carbon films were examined by Raman spectroscopy, atomic force microscopy (AFM), scanning electron microscopy, X-ray photelectron spectroscopy, ellipsometry, cyclic voltammetry (CV), etc.

The carbon films obtained by thermal pyrolysis of photoresist on Si wafers are atomically smooth (*i.e.*, surface roughness of about 30 Å was determined by AFM). The carbon films prepared at temperatures ≥700°C showed electrochemical behavior (CV, $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox couple) similar to that of glassy carbon.[4,5] Furthermore, the electrochemical properties of the carbon film electrodes are very stable, exhibiting reproducible behavior even after storing at room temperature in air for 3 months.

In addition to the electrochemical studies of carbon films, we embarked on an effort to fabricate microelectrodes that may be useful for microbattery or sensor applications. Interdigitated electrode (IDE) arrays of carbon microelectrodes were fabricated by classical semiconductor techniques.[1-3] In this process, thin layers of photoresist are spin coated on Si wafers, and the desired IDE arrays are obtained by use of a suitable mask and photolithographic patterning. After UV exposure and development, the patterned photoresist on Si wafer is thermally pyrolyzed to convert the photoresist to carbon to form the IDE array. The typical dimensions of the carbon microstructures are ~500 μm digit lengths, ~50 μm digit widths, and a distance between digits of ~10 μm. These carbon IDEs are thin carbon films (<10 μm thick) that are essentially two-dimensional structures. One of the time-consuming and costly tasks in this procedure is the design and fabrication of the photomasks used to obtain the IDE arrays. Any change in the geometric pattern of the microelectrode array requires a different mask, and this is a major limitation in the design of interdigitated carbon microelectrodes. Therefore, we developed a more rapid process for designing and patterning carbon IDE arrays that involved using a laser beam to pyrolyze (laser pyrolysis) the photoresist.

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Experimental

The preparation and characterization of carbon films obtained by heat-treatment of photoresist on Si wafers (10 cm diam) were described by Kinoshita and co-workers.[4,5] A positive photoresist (OiR 897-101, Olin Corp., Norwalk, CT) was used to produce the carbon films. This photoresist consists of predominantly novolak resins, according to the Material Safety Data Sheet information provided by the manufacturers. Further analysis to determine the chemical composition was not performed.

An extension of the procedure used to produce carbon films was employed to form the carbon IDEs on Si wafers. In this case, additional processing steps involving micropatterning and photolithography of the photoresist were required. These steps were carried out at the Microfabrication Facility in the Electronics Research Laboratory at the University of California at Berkeley. A procedure to produce the carbon IDEs by thermal pyrolysis is described in detail elsewhere.[1,2]

An integrated Raman microscope system Labram by ISA Groupe Horiba was used for laser pyrolysis of the photoresist, and also to analyze the structure of the carbonaceous product. The excitation wavelength was supplied by either an internal HeNe (632 nm), 20 mW laser or an external Ar-ion (514 nm), 2 W laser. The power of the laser beam was adjusted to the required levels with neutral filters of various optical densities. The size of the laser beam at the sample surface can be varied from 1.6 to several hundred micrometers, and it is controlled by the characteristics of the microscope optics and the distance between the sample and objective lens. The diameter of laser beam applied in our experiments was 5 μm. To control the position of the sample with respect to the laser beam, a motorized XY microscope stage of 0.1 μm resolution and 1 μm reproducibility was used. The exposure time of the photoresist to the laser beam was controlled by either the XY stage motion speed, or a digital laser beam shutter (model 845 HP by Newport Corp.), which was used in static experiments.

Results and Discussion

Simple schematic representations of the processing steps in photolithography and laser lithography used to fabricate microelectrode arrays by thermal pyrolysis and laser pyrolysis, respectively, are illustrated in Fig. 1. In thermal pyrolysis, the Si wafer is placed in a Lindberg furnace after spin coating and baking, purged with He, and heated at a rate of 5°C/min to the desired temperature to pyrolyze the photoresist. The sample is held at the pyrolysis temperature for 1 h and then cooled to room temperature. A rapid heating rate is not desirable because the carbon films do not adhere well to the substrate if thermal pyrolysis occurs too rapidly. Thus, the thermal cycle to produce a carbon film can take many hours.

Optical microscopy and interferometry studies[2] of the microstructure and 3-D surface topography of carbon IDEs showed that the width of the digit shrinks by ~20% when the photoresist is pyrolyzed at 1000°C. The interdigitated structures of the patterned

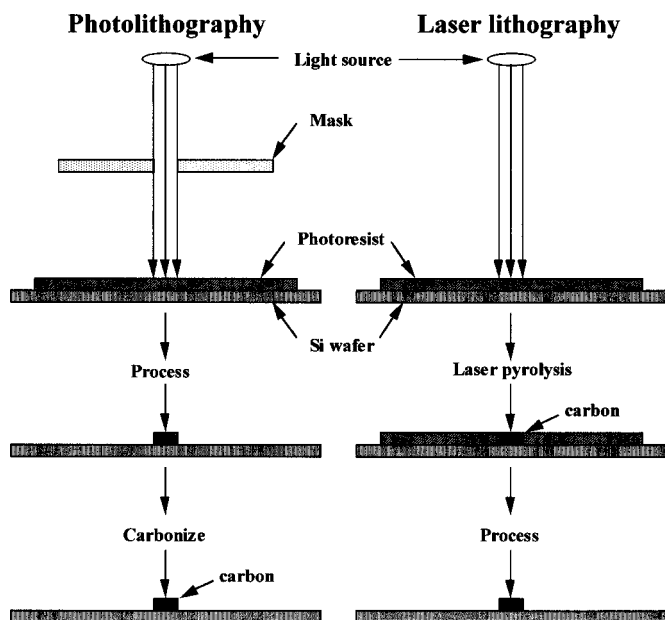**Photolithography**   **Laser lithography**

Figure 1. Schematic representation of the processing steps used in photolithography and laser lithography to fabricate the microelectrode arrays by thermal pyrolysis and laser pyrolysis.

Figure 2. Raman spectra of carbon film obtained by thermal pyrolysis (A) followed by laser pyrolysis with 10 mS pulse and 1 W power at 514 nm (B).

phototresist have surface profiles that are more rectangular in shape prior to heat-treatment. However, after thermal pyrolysis, the digits appear to have a profile that resembles an inverted cone, which are wider at the base in contact with the Si wafer and narrower at the top. The region near the top of the digit is free to shrink and changes volume when the sample is slowly heated and as the photoresist passes from a solid state to a softened/melted state.

The main differences in the two procedures are the elimination of the mask and thermal treatment when laser pyrolysis is used. Controlling the motion of the sample by computer software allows one to design a wide variety of microelectrode arrays. This flexibility is a major advantage over photolithography using a mask pattern. The power density of the laser beam must be controlled to avoid vaporizing the photoresist without converting it to carbon or to minimize the loss of carbon by laser ablation, for example. Ouyang and Hiraoka[11] demonstrated that polybutadiene can be laser ablated in hydrogen to form a diamond-like carbon using an excimer laser (193 nm). When laser pyrolysis is conducted in air, the laser power must be held at a suitable level to avoid excessive heating of the carbon to minimize oxidation. This problem can be avoided by exposing the photoresist to the laser beam in an inert environment.

A typical Raman spectrum of carbon film obtained by thermal pyrolysis of the photoresist at 800°C is shown in Fig. 2a. The origin of two major Raman bands at approximately 1360 and 1580 cm^{-1} has been discussed extensively,[2,7,8] and is not elaborated here. The peak profiles of the carbon obtained by thermal pyrolysis are broad, indicating significant contribution from disordered sp2 and sp3 carbon structures. Interestingly, when the carbon is exposed to a 10 ms pulse from a 1 W laser at 514 nm, a marked change in the Raman spectrum is observed. The thermal energy from the laser beam heats the surface and induces a change in the carbon structure. The Raman spectrum obtained after exposure to the laser beam shows that both the D and G carbon bands become much narrower, and they more closely resemble the spectrum of more ordered carbon films produced at higher thermal-pyrolysis temperatures. These results indicate that the laser beam delivered sufficient thermal energy to promote further changes in the original carbon structure that was produced by thermal pyrolysis at 800°C.

The Raman spectra of carbons obtained by irradiation at different power levels from a 514 nm laser beam is presented in Fig. 3. Four
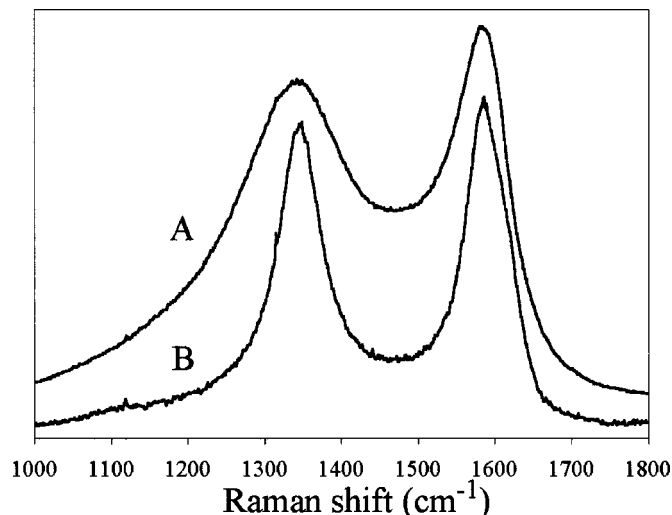
layers of a positive photoresist were spin coated on a Si wafer and then baked at 150°C. The photoresist was exposed for a couple of seconds in air at room temperature to a laser beam with controlled power ranging from 21 to 920 mW. Laser pyrolysis produced carbon structures of 2 μm diam at 21 mW to 40 μm diam at 920 mW. The increase in the diameter of the carbon suggests that the thermal energy from the laser beam at higher power levels induces pyrolysis over a wider area than that expected from the beam diameter (2 μm). However, the size of the laser beam remained constant and independent of the laser power. A high-power laser beam delivered an excess of energy that could not be dissipated fast enough by the carbon and the silicon substrate. Consequently, it produced a larger pyrolysis zone in the photoresist film. The calculated power density at 920 mW did not exceed 2.94×10^7 W/cm^2, which is still considerably lower than those required for pulse laser ablation of graphite. As a point of reference, peak power densities ranging from 2 to 9×10^9 W/cm^2 with a Q-switched Nd-YAG laser (1064 nm) were used by Moon *et al.*[9] for laser ablation of graphite.

The results in Fig. 3 show that carbons obtained at low power have Raman spectra with broad D and G bands at ~1360 and 1580
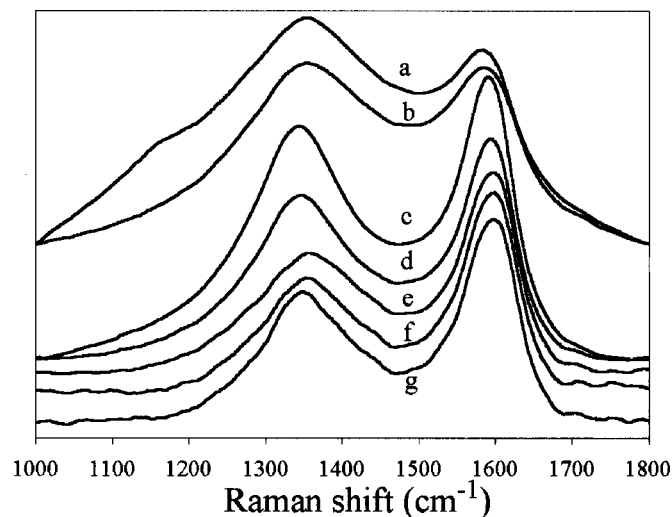

Figure 3. Raman spectra of carbon obtained by exposing a positive photoresist to (a) 21, (b) 62, (c) 120, (d) 190, (e) 380, (f) 730, and (g) 920 mW laser beam for 5 s.
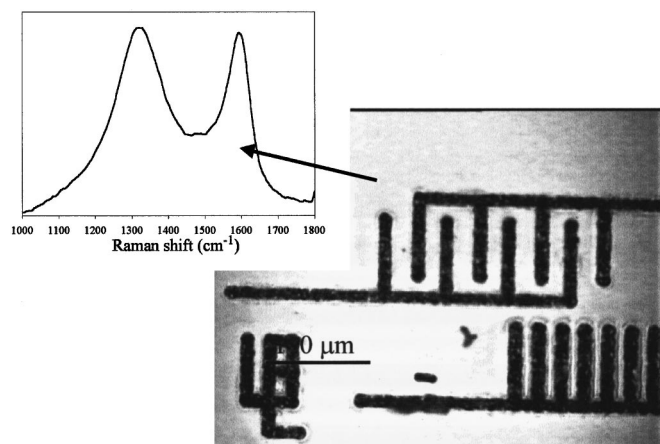
Figure 4. Optical image of carbon structure obtained by laser pyrolysis to produce carbon from a positive photoresist. The inset shows a Raman spectrum of the carbonaceous product.

cm^{-1}, respectively. These peaks become progressively sharper, and their relative intensities ratio (I_{1360}/I_{1580}) decreases as the laser power increases to 920 mW. These changes in the Raman spectra suggest that a more graphitic-type of carbon is formed at higher laser power. However, deconvolution of the Raman bands indicate that the peak at 1622 cm^{-1} which contributes to the G-band also becomes more prominent at higher laser power, and correspondingly, at higher pyrolysis temperature. The Raman peak at 1622 cm^{-1} is typical for disordered carbonaceous materials with -OH, -CHO, -COOH function groups adsorbed at the surface.[10]

An optical image is presented in Fig. 4 to illustrate the results obtained by laser pyrolysis to produce carbon structures from a positive photoresist. A laser operating at 632 nm, and with a 5 μm beam size and 8 mW power, was used to produce the carbon patterns. Computer software was used to control the movement of the sample to form the carbon configurations. The speed of the movement of the XY motorized sample stage was 8 mm/s. The width of the digits in the interdigitated structure is about 20 μm. It is slightly wider than the carbon path that connects them because each finger was exposed twice to the laser beam. A Raman spectrum of carbon at a location on one of the digits is shown in the inset of Fig. 4. It is remarkably similar to that obtained by thermal pyrolysis of the same photoresist at 1000°C. Despite the fact that the type of carbon and its properties that are produced by laser pyrolysis of photoresist have not been optimized, these preliminary results demonstrate that carbon microelectrodes with Raman spectra comparable to those obtained by heat-treatment are readily produced. Future effort will involve measurements to determine the electrochemical response of the carbon microelectrodes obtained by laser pyrolysis.

No effort was undertaken to analyze the detailed mechanisms to explain laser pyrolysis. However, theoretical studies of pulse laser ablation provide some insight to the phenomena occurring when a solid is irradiated. Zhigilei and co-workers[12-14] presented a physical picture from simulation studies of laser ablation. The wavelength and power of the laser light, as well as the pulse duration, affect the energy, penetration depth, and the number of molecules that are excited. It is expected that these parameters also impact laser pyrolysis; however, more analysis is needed to provide a clear explanation. The experimental conditions for rapid formation of carbon by laser pyrolysis have not been optimized. Therefore, the appropriate laser power and exposure time of the photoresist to minimize softening, deformation, and structural change before carbonization occurs are not well defined. These issues will be investigated in more detail in the future.

Conclusions

The Raman spectra indicate that the carbon properties can be controlled by varying the beam power of the laser. Although this technique was not optimized, the use of a laser beam to pyrolyze a photoresist to form a well-defined electrode array was demonstrated.

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